Spectroscopic Study of Water Vapor Absorption in the 8- to 14-μm Atmospheric Window: Measurement of New Line and Continuum Parameters and Investigation of Far-Wind Phenomena

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The accurate quantitative understanding of the latent infrared (IR) absorption in the atmospheric window regions continues to be an area of research interest for the global climate modeling community. This need is particularly great in the 8- to 14-μm window, which spans a large portion of the 300K blackbody emission spectrum. There, the latent absorption is caused primarily by water vapor and consists of two distinct features: 1) the weak lines originating both from transitions in the far edge of the water pure rotational band (at the long wavelength boundary of the window) and from transitions located in the trailing edge of the υ_2 rovibrational band (at the short wavelength boundary) and 2) the water vapor continuum. The database concerning the lines is periodically updated, yet there remain spectral gaps in which accurate laboratory measurements are required to substantiate long-pathlength atmospheric results.

The continuum has been the subject of investigations for a number of years, both with respect to its spectral intensity as a function of temperature and pressure and with regard to its physical origins. At present, the continuum absorption near room temperature is relatively well characterized; however, the database must be expanded to span all relevant atmospheric conditions. Among the explanations proposed as causes of the continuum are the cumulative absorption of the far wings of distant lines, absorption by dimers and higher-order clusters, and higher-order linear absorption processes. A common thread among all these explanations is that the continuum absorption is somehow linked to intermolecular interactions between water molecules.

The initial goals of this project are to address the gaps in the quantitative understanding of both the water vapor line and continuum absorption in the 8- to 14-μm window. To this end, the initial year has been spent assembling the necessary equipment to make these measurements (and to support other Atmospheric Radiation Measurement [ARM] laboratory spectroscopic needs, as they arise). This effort consisted primarily of designing and constructing a multipass absorption cell and the chamber to house the cell, assembling the spectroscopic instrumentation necessary to make the measurements, and adapting these instruments to operate in conjunction with the multipass cell. The spectroscopic instruments to be used consist of a diode laser spectrometer, operated in the sweep integration mode (to measure line absorption), and a BOMEM MB100 Fourier Transform infrared [FTIR] spectrometer (for continuum measurements).

The multipass cell that is used in this project is of the Horn-Pimentel design and has a maximum pathlength of at least 300 m, with a base pathlength of 3 m. The cell is a commercially available item, obtained from Infrared Analysis, Inc (Anaheim, California). The cell mirror surfaces are composed of ceramic-coated Ag and have specified reflectances of 99.5% in the regions of interest. Because the cell pathlength is shorter than those used in earlier studies, it is essential that the stability of the cell optics and the conditions within the chamber housing the cell be controlled to high precision. Also, the shorter pathlength places greater constraints on the stability of the spectroscopic instruments that are used to make the measurements, particularly with regard to the continuum absorption. This concern will be addressed by taking advantage of the exceptional baseline stability of the MB100 spectrometer, which is nearly an order of magnitude greater than that of other, similar instruments. An

advantage afforded by the smaller cell, apart from the obvious space considerations, is the ability to create a more homogeneous gas sample than was possible in earlier, longer systems.

In addition to stability, several other issues must be addressed when making spectral measurements of water vapor. These arise primarily as a result of the difficulty in creating and handling mixtures of air and water vapor. Fortunately, because of the number of past attempts to measure the spectral properties of water vapor, there is a considerable amount of information in the literature regarding these problems, which result primarily from the low saturation vapor pressure of water at room temperature. As a result of its low saturation pressure, water easily condenses onto container walls, mirrors, and transmission windows. Another aspect of the adsorption problem is the need to equilibrate the vapor-phase water with that adsorbed on the walls of the cell container, so that a stable vapor concentration may be obtained. Because of adsorptive losses, it is necessary to have an independent means of measuring water partial pressure within the cell. Finally, the water vapor and the diluent gas must be adequately mixed to prevent refractive inhomogeneities within the cell that will lead to beam wander and, thus, erroneous results.

These concerns influenced the design of the chamber to house the multipass cell (Figure 1). The chamber is being constructed in three separate segments of stainless steel, with a highly polished inner wall. Stainless steel has been used successfully in the past to contain stable water vapor mixtures, and the smoothness of the inner walls will minimize the surface area available for adsorption. Optical stability is enhanced by supporting the entire assembly on a granite slab, which will isolate the optics from room vibrations and will minimize the effects of room temperature fluctuations on the intermirror spacing. Isolation of the mirrors from movement of the chamber walls that may arise during the evacuation of the cell is accomplished by attaching the mirror mounts to the support independently of the chamber. Although both the cell and the optics are mounted to the same steel plate, that plate is rigidly attached to the granite in many places, so that it effectively serves as an extension of the granite surface.

Thermal control of the inner environment of the chamber is accomplished by circulating a heat-exchange fluid through a jacketed reservoir that surrounds each of the three segments of the chamber. Each jacket is connected in parallel to an FTS model RC-200-ULT temperature controller. Thermal insulation from the surroundings is provided by a layer of Armaflex insulation. Temperature will be monitored within the cell at four different places using thermistors. Given the specifications of the temperature controller and of the chamber, it is expected that temperatures between -40° and 60°C will be attainable, without having to change fluids. Thermal control of the optical surfaces is accomplished separately using Kaptan contact heating elements that are affixed to the components and controlled by separate heater control modules.

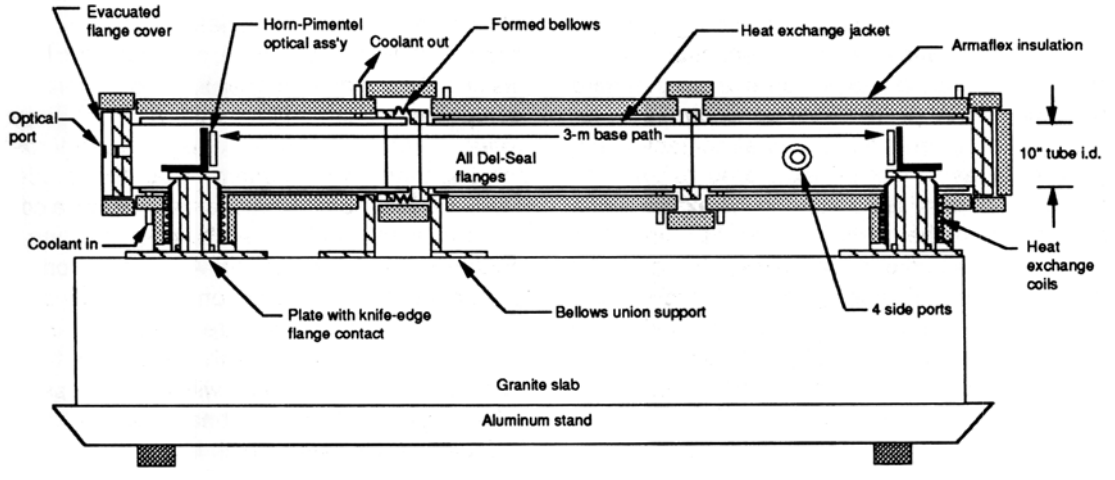

Figure 1. Diagram of the Horn-Pimentel multipass cell and chamber.

The mixture of the appropriate water vapor samples is accomplished using a diluent gas distributor, located at the top of the chamber volume. Water vapor introduced into the cell is mixed with the diluent gas, which is introduced in many locations in the cell rather than only from one end. This prevents stratification of the vapors. Additionally, recirculating fans will be placed within the cell to further stir the mixture. Once the gas mixture has been created, water vapor concentration will be monitored using an EG&G Model 880 dewpoint hygrometer. As the work progresses, the feasibility of monitoring the water vapor concentration using the intensity of a water vapor line will also be investigated, as this will provide a measurement that is more representative of the entire chamber volume.

At the present time, the cell chamber is being constructed by MDC Corporation (Hayward, California). The diode laser spectrometer has been made operational, and the mechanism for coupling it and the MB100 FTIR to the multipass cell has been designed. When the completed chamber is received (expected in mid-November), the apparatus will be assembled, and water vapor measurements will subsequently begin.